

Density Functional Based Vibrational Study of Conformational Isomers: Molecular Rearrangement of Benzofuroxan

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ABSTRACT: The molecular rearrangement of benzofuroxan was studied by comparing calculated and experimental IR spectra, the latter taken before and during the reaction. All calculations were performed at the B3-LYP/6-31G(*d*) density functional level with a further refinement of the computed force constants done by applying the scaled quantum mechanical force field (SQM) technique. Complete assignments for the IR spectra of benzofuroxan and nitrosobenzene are given. The agreement between computed and experimental spectra is excellent, but in benzofuroxan these spectra are very different from previously calculated data. The conformation of the *ortho*-dinitrosobenzene intermediate of this tautomeric reaction was identified by modeling a composite IR spectrum of four possible components. It shows good agreement with an experimental spectrum that was obtained after photolysing benzofuroxan in Xe matrix. Knowing the conformation of the intermediate provides insight into the reaction mechanism and allows inferences for the thermal reaction, which could not be clarified conclusively by energetic considerations only. © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 489–500, 1997

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Introduction

Recent experimental and theoretical studies of the molecular rearrangement of benzofuroxan provide very strong evidence that 1,2-dinitrosobenzene is the most likely intermediate of this tautomeric reaction¹ (Fig. 1). This conclusion was drawn experimentally from ¹H NMR studies as well as UV and IR spectra. Three groups independently measured the IR spectrum of this photochemically induced reaction in Xe and Ar matrix isolation.^{2–4} The occurrence of a number of new bands in the IR spectrum of photolysed benzofuroxan (which from now on we will call the reaction spectrum) was assigned to *ortho*-dinitrosobenzene. Several groups theoretically investigated a certain number of possible intermediates and reached the same conclusions.^{5,6}

However, so far the preferred conformation of the 1,2-dinitrosobenzene intermediate and thus the exact reaction mechanism are still a subject of discussion. Theoretical studies tend to favor the *trans,trans* conformer, but recently we showed that the *cis,trans* and *trans,trans* conformers are almost equal in energy [$\Delta E = 0.2$ kcal/mol at the B3-LYP/6–311G(*d, p*) level].⁷ Because these energetic considerations are not absolutely conclusive with respect to the preferred mechanism and structure of the intermediate observed, in this study we tried to reproduce the experimentally obtained IR spectrum of Hacker² who measured an IR spectrum at 14 K in a xenon matrix after photolysing benzofuroxan for 2 h at 366 nm.

The task to reproduce his spectrum solely from *ab initio* data is rather complex, because several conformers of 1,2-dinitrosobenzene and the educt and product, benzofuroxan, may contribute to the experimental spectrum. On the other hand it is also rather challenging to identify the composition

of a reaction spectrum simply from calculated data, because this opens the way to analyzing unknown IR spectra by automated computational data base approaches, even for conformational problems. Using IR spectra as an interface between theory and experiment is only possible because the quality of calculated spectra increased significantly with further improvements in *ab initio* and density functional theory (DFT) during the last decade.

After discussing some computational details, we explain a set of scaling factors that we derived to correct our calculated vibrational force fields for anharmonicity, correlation, and basis set deficiencies effects. Then we discuss our calculated spectra of benzofuroxan and nitrosobenzene that were used to obtain the set of scaling factors and compare our results with experimental data. Finally we try to identify the composition of the reaction spectrum of Hacker² from our calculated spectra of benzofuroxan and all three conformers of 1,2-dinitrosobenzene.

Computational Aspects

In this study we used the scaled quantum mechanical force field procedure (SQM)⁸ in combination with DFT derived vibrational force fields.⁹ Specifically, we used the three parameter exchange–correlation functional of Becke¹⁰ and Lee–Yang–Parr¹¹ (B3-LYP) throughout. It has been shown recently that this functional together with the SQM procedure reproduces experimental spectra to a high accuracy.¹² The SQM method simply scales a given vibrational force field by a set of scaling factors, according to

$$\mathbf{F}' = \mathbf{C}^{1/2} \mathbf{F} \mathbf{C}^{1/2}, \quad (1)$$

where \mathbf{F} is the original force constant matrix and \mathbf{C} the diagonal matrix of scaling factors. Furthermore, each scaling factor belongs to a class of natural internal coordinates¹³ that usually limit the

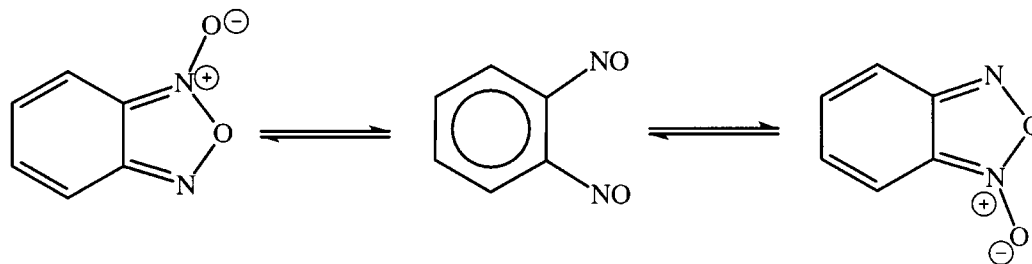


FIGURE 1. The molecular rearrangement of benzofuroxan.

number of factors to 8–10. A detailed description of the procedure, which is much superior to a uniform scaling of frequencies, is given in ref. 8.

All geometries were optimized at the 6–31G(*d*) level,¹⁴ which is a smaller basis than the 6–311G(*d*, *p*) basis set¹⁵ we used in our first study.⁷ We used this basis now in order to apply our transferable scaling factors (TSF)¹² within the SQM procedure, which are only available for B3-LYP/6–31G(*d*) derived force fields (see below). We attempted to use the same scaling factors for the larger basis set but the reproduction of the frequencies became less accurate. The geometry differences between the two basis sets were small and the calculated structure of benzofuroxan was in good agreement with experimental X-ray data^{16,17} (see Table I). The labeling of the atoms is given in Figure 2.

The calculated geometrical parameters show the same tendencies as discussed in our first article.⁷ Consequently, it is sufficient to mention that the most critical bond, the endocyclic N—O bond, which causes severe problems ($\Delta r > 0.1$ Å) at the Hartree–Fock (HF) or the second-order Møller–Plesset (MP2) level,^{5,7} is well represented by the B3-LYP/6–31G(*d*) geometry. Therefore, the requirement of a good reproduction of the experimental geometry, which is essential for a vibrational study, is given. There was an attempt to assign the fundamentals of benzofuroxan based on an HF calculation,⁵ but the error in the geometry led to large errors in the calculated frequencies

and what we consider to be a number of misassignments. Because of its strong tendency to dimerize,¹⁸ X-ray data for the nitrosobenzene monomer, which will be discussed in detail too, are not available, to the best of our knowledge.

All calculations were performed on IBM RS6000 workstations using the G92/DFT suite of programs¹⁹ and our SQM program.^{20,21}

Scaling Factors

Recently, based on a training set of 20 small organic compounds, a set of TSFs for B3-LYP/6–31G(*d*) computed force fields was established in our group. Because these scaling factors had to be fit to experimental data, the molecules in that set were selected carefully in order to have experimentally well characterized fundamentals. Using these scaling factors on 11 other test molecules proved the transferability of these factors.¹² The corrections provided by TSFs cannot be expected to be accurate for the force constants of unusual structural units which were not included in the training set. The best solution for cases like this is to introduce new scaling factors based on similar molecules, the fundamentals of which are securely assigned. Benzofuroxan with its furazan ring as well as the dinitrosobenzene conformers belong to this kind of molecules for which the TSFs have major limitations. None of the com-

TABLE I.
Calculated and Experimental Geometrical Parameters of Benzofuroxan (C_6).

<i>r</i>	Calcd	Exptl	\angle	Calcd	Exptl
N ₁ —O ₁	1.223	1.235	C ₁ —N ₁ —O ₁	134.9	136.7
N ₁ —O ₂	1.448	1.464	C ₁ —N ₁ —O ₂	105.6	106.7
N ₂ —O ₂	1.371	1.381	N ₁ —O ₂ —N ₂	109.9	108.2
C ₁ —N ₁	1.343	1.319	C ₂ —N ₂ —O ₂	105.8	105.9
C ₂ —N ₂	1.326	1.327	C ₁ —C ₂ —N ₂	111.6	111.9
C ₁ —C ₂	1.425	1.418	C ₂ —C ₁ —N ₁	107.1	107.3
C ₂ —C ₃	1.429	1.416	C ₄ —C ₃ —H ₁	122.5	(119)
C ₃ —C ₄	1.369	1.347	C ₅ —C ₄ —H ₂	118.1	(117)
C ₄ —C ₅	1.440	1.441	C ₆ —C ₅ —H ₃	119.7	(128)
C ₅ —C ₆	1.370	1.337	C ₁ —C ₆ —H ₄	120.5	(120)
C ₆ —C ₁	1.416	1.426	C ₁ —C ₂ —C ₃	119.0	119.8
C ₃ —H ₁	1.084	(0.95)	C ₂ —C ₃ —C ₄	117.3	117.4
C ₄ —H ₂	1.086	(1.04)	C ₃ —C ₄ —C ₅	122.6	122.2
C ₅ —H ₃	1.086	(0.96)	C ₄ —C ₅ —C ₆	121.6	122.3
C ₆ —H ₄	1.084	(0.87)	C ₅ —C ₆ —C ₁	116.1	116.3
			C ₆ —C ₁ —C ₂	123.3	122.0

Bond lengths in Ångströms and angles in degrees.

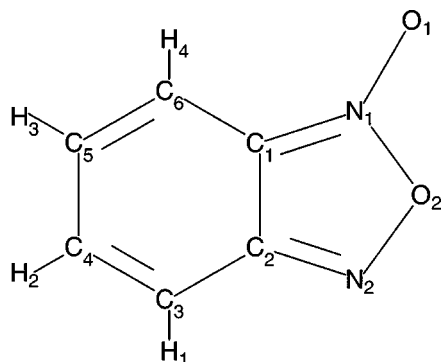


FIGURE 2. The atomic numbering of benzofuroxan.

pounds from the 20-molecule set included a furazan ring or the nitroso group; therefore, the need for new scaling factors for our study was obvious. To establish a new set of scaling factors we used the experimentally securely assigned fundamentals of benzofuroxan^{3,4} and nitrosobenzene.²² The initial spectra predicted for these two molecules using TSFs were accurate enough ($\leq 22 \text{ cm}^{-1}$) to establish the identity of the calculated fundamentals in the scaling factor refinement. As shown in the next sections, the optimized scaling factors excellently reproduce the experimental spectra of benzofuroxan and nitrosobenzene. Because of strong structural similarities between these molecules and 1,2-dinitrosobenzene, we expected that these factors would be appropriate for the conformers of the latter. To minimize the number of new parameters, the scaling factors corresponding to the six-membered ring, such as CH stretchings and bendings as well as ring deformation, were taken unchanged from the set of TSFs. The need for new scaling factors, as expected, mainly concerned the NO active vibrational modes. The

scaling factors optimized for these molecules differ only slightly from the TSFs. Table II compares the two sets. The extra freedom in the present set results in lower scaling factors for the NO stretchings and the CCNO torsions, and higher factors for the modes to which they are coupled: CC and CN stretchings and ring torsions.

The calculated frequencies and intensities of benzofuroxan, nitrosobenzene, and all three conformational isomers of 1,2-dinitrosobenzene, using the scaling factors discussed above, are shown in Tables III, IV, and V,²³ respectively.

IR Spectrum of Benzofuroxan

The 36 fundamental vibrations of benzofuroxan within the C_s point group can be classified as 25 in-plane modes (a') and 11 out of plane modes (a''). All fundamentals are expected to be IR active. We compare our SQM results with an experiment²⁻⁴ as well as with previous theoretical studies⁵ at the restricted Hartree-Fock/double-zeta polarization (RHF/DZP) level, using a uniform frequency scaling factor of 0.91. Not all fundamentals in the experimental^{3,4} and previous theoretical vibrational spectra of benzofuroxan have been identified or assigned. The missing assignments for the low frequency region (below 550 cm^{-1}) are probably due to very weak signals. The experimentally strongest bands of the spectrum are at 1622 and 1598 cm^{-1} . The SQM calculation places these in-plane vibrations at 1633 and 1607 cm^{-1} , respectively. The stretching of the polar exocyclic NO bond in these vibrations is responsible for their high intensities. There are a few small disagreements between calculated and experimental

TABLE II.
Scaling Factors Obtained from Fitting Calculated Frequencies to Experimental Fundamentals of Benzofuroxan and Nitrosobenzene and Corresponding Transferable Scaling Factors.

No.	Internal Coordinate	Scale Factor	Corresp. TSF
1	CC and CN stretching	0.936	0.922
2	NO stretching	0.890	0.922
3	CH stretching ^a	0.920	0.920
4	Heavy atom bending CCC, CNO, CCN ^a	0.990	0.990
5	CCH bending ^a	0.950	0.950
6	Hydrogen out of plane modes ^a	0.976	0.976
7	Ring torsions	0.986	0.935
8	CCNO torsions and out of plane modes	0.725	0.831

TSF, transferable scaling factor.

^a Not individually optimized for benzofuroxan and nitrosobenzene.

TABLE III.
Calculated and Experimental Vibrational Frequencies (cm^{-1}) and Intensities (km / mol) of Benzofuroxan.

No.	Symmetry	Calcd	Int.	Exptl ^{a,b}	Exptl ^{b,c}	Assignment
1	a''	160.1	1.0			Ring twist (out of plane)
2	a''	193.8	0.1			Butterfly vibration
3	a'	283.8	0.9			Ring twist (in plane)
4	a''	327.4	2.7			Boat and envelope def.
5	a''	422.7	2.5			Boat def.
6	a'	467.4	1.1			Furazan ring opening
7	a''	473.1	2.5			6 memb. ring squeezing
8	a'	523.4	1.5			Envelope and boat def.
9	a''	559.4	1.0		563 (w)	Envelope and twist-boat def.
10	a'	572.3	9.9		574 (m)	Ring def. (in plane)
11	a'	670.5	6.5	669 (w)	666 (w)	Furazan ring open. and 6 memb. ring def.
12	a''	740.7	0.7	739 (w)	737 (m)	Twist-envelope and twist-boat def.
13	a''	747.9	61.8	746 (m)	746 (m)	H out of plane (+, +, +, +) ^d
14	a'	761.7	3.8	760 (w)		6 memb. ring breathing
15	a'	825.5	5.5	837 (w)	833 (w)	Antisymm. endo-NO stretching
16	a''	846.6	0.4			H out of plane (+, +, -, -) ^d
17	a'	895.3	10.2	895 (w)	892 (w)	Ring def.
18	a''	952.9	0.2			H out of plane (+, -, -, +) ^d
19	a'	973.9	1.3			$\text{C}_4\text{—C}_5$ stretching and H def.
20	a''	986.0	0.0			H out of plane (+, -, +, -) ^d
21	a'	1021.0	53.1	1020 (m)	1017 (m)	Symm. endo-NO stretching
22	a'	1121.2	5.7	1126 (w)	1122 (w)	CCH bending i.p.
23	a'	1151.7	1.2	1151 (vw)		CCH bending i.p.
24	a'	1200.6	9.3	1205 (w)	1202 (w)	CCH bending i.p. and CN stretching
25	a'	1286.3	1.9			CCH bending i.p.
26	a'	1366.6	1.9	1358 (w)	1354 (w)	CCH bending i.p. and CN stretching
27	a'	1415.2	8.7	1427 (w)	1424 (w)	$\text{C}_5\text{—C}_6 / \text{C}_3\text{—C}_4$ stretching
28	a'	1450.0	5.1	1446 (w)	1444 (w)	$\text{C}_4\text{—C}_5 / \text{C}_1\text{—C}_2$ stretching
29	a'	1505.1	24.1	1492 (m)	1489 (m)	CN and CC stretching
30	a'	1547.0	55.3	1545 (s)	1545 (s)	$\text{C}_4\text{—C}_5 / \text{C}_1\text{—C}_2$ stretching
31	a'	1606.5	206.3	1598 (s)	1597 (s)	$\text{C}_5\text{—C}_6 / \text{C}_3\text{—C}_4$ and exo-NO stretching
32	a'	1633.1	286.8	1622 (s)	1622 (s)	CN and exo-NO stretching
33	a'	3069.1	6.9			Antisymm. CH stretching
34	a'	3082.7	6.2			Symm. CH stretching
35	a'	3099.5	3.4			Antisymm. CH stretching
36	a'	3103.7	3.9			Symm. CH stretching

^a Taken from ref. 3.^b s, strong; m, medium; w, weak; vw, very weak.^c Taken from ref. 4.^d (+, -) The phase of the motion for the four hydrogens.

frequencies, especially for weak in-plane modes: 1358 (expt) vs. 1367 cm^{-1} (calcd), 1427 (expt) vs. 1415 cm^{-1} (calcd), and 837 (expt) vs. 826 cm^{-1} (calcd). The medium band at 1492 is calculated to be at 1505 cm^{-1} . Although these deviations are relatively high for the SQM technique, the overall reproduction of the experimental spectrum is excellent (Table III, Fig. 3).

The weak band seen in the experimental spectrum at about 1528 cm^{-1} has not been assigned as a fundamental and is most likely a combination

band. The frequencies of the two out of plane bands calculated at 741 and 748 cm^{-1} are in excellent agreement with their experimental positions at 739 and 746 cm^{-1} , respectively. However, their calculated intensities do not correspond to the experimentally assigned medium intensity for both bands. The 741 cm^{-1} band is very weak, but the 748 cm^{-1} must be considered as strong. Because the frequencies of these modes are very close and they are of the same symmetry (a''), the most probable explanation for this discrepancy is that

TABLE IV.
Calculated and Experimental Vibrational Frequencies (cm^{-1}) and Intensities (km / mol) of Nitrosobenzene.

No.	Symmetry	Calcd	Int.	Exptl ^{a,b}	Assignment
1	a''	103.5	0.2	101 (vw)	CCNO torsion
2	a''	226.0	0.4	200 (w)	N out of plane
3	a'	252.7	2.3	254 (s)	X bend
4	a''	416.2	0.0	420 (vw)	Twist def.
5	a'	440.5	0.8	438 (vw)	Ring breathing and CN stretching
6	a''	448.2	0.4	458 (w)	Boat def.
7	a'	619.6	0.2		Ring def.
8	a'	674.2	10.1		Ring breathing and CNO bending
9	a''	693.6	15.0	682 (vs)	Chair def.
10	a''	760.0	50.8	750 (vs)	H out of plane (+, +, +, +, +) ^c
11	a'	818.3	32.3	812 (vs)	CNO bending and CN stretching
12	a''	859.2	0.0	850 (s)	H out of plane (+, +, 0, -, -) ^c
13	a''	944.5	2.7	933 (s)	H out of plane (+, 0, -, 0, +) ^c
14	a''	980.0	0.0		H out of plane (+, -, 0, +, -) ^c
15	a'	998.4	2.1	997 (vw)	Symm. ring def.
16	a''	999.0	0.1	1002 (w)	H out of plane (+, -, +, -, +) ^c
17	a'	1014.3	8.3	1018 (s)	CCH bending i.p.
18	a'	1071.7	4.2	1067 (vw)	CCH bending i.p.
19	a'	1108.8	139.8	1112 (vs)	CN stretching and CCH bending i.p.
20	a'	1161.2	0.9	1158 (vw)	CCH bending i.p.
21	a'	1172.9	12.5	1176 (s)	CN stretching and CCH bending i.p.
22	a'	1310.2	9.2	1314 (s)	CCH bending i.p.
23	a'	1334.1	14.8	1348 (vw)	Symm. CC stretching
24	a'	1450.1	59.8	1455 (s)	CC stretching and CCH bending i.p.
25	a'	1472.5	11.9	1477 (w)	CC stretching and CCH bending i.p.
26	a'	1525.7	144.1	1523 (vs)	NO stretching
27	a'	1603.6	1.0		Symm. CC stretching
28	a'	1608.5	1.3	1615 (w)	Symm. CC stretching
29	a'	3058.6	0.6	3052 (vw)	CH stretching
30	a'	3069.8	9.9		CH stretching
31	a'	3077.1	14.1	3080 (s)	CH stretching
32	a'	3086.5	11.8		CH stretching
33	a'	3094.5	4.8		CH stretching

^a Taken from ref. 22.

^b s, strong; w, weak; vw, very weak; vs, very strong.

^c (+, -) The phase of the motion for the five hydrogens.

small coupling terms in the force field may strongly affect the mixing of these vibrations and thus their relative intensities.

Benzofuroxan is a typical non-Hartree-Fock molecule, and it is thus not surprising that its IR spectrum cannot be accurately reproduced at the self-consistent field (SCF) level (see ref. 5 and our spectrum in Fig. 3). The differences between theoretical and experimental frequencies are up to 70 cm^{-1} . This is mostly due to the poor reproduction of the molecular geometry at the HF level. The IR spectrum calculated at the HF/6-311G(*d*, *p*) level and uniformly scaled (similar to the one in ref. 5) differs dramatically from the experimental and the SQM/DFT spectra. From the comparison in Figure

3 it is apparent that an assignment at this level is questionable, even more so because the intensities do not match at all.

IR Spectrum of Nitrosobenzene

Nitrosobenzene was chosen as a second reference molecule for deriving new scaling factors for two reasons: first because of its structural and vibrational similarities with conformers of 1,2-dinitrosobenzene and second because its experimental fundamentals have been carefully identified and assigned.²²

TABLE V.

Calculated Vibrational Frequencies (cm^{-1}) and Intensities (km / mol) of *trans,trans*-, *cis,trans*-, and *cis,cis*-Dinitrosobenzene.

No.	<i>trans,trans</i> -DNB			<i>cis,trans</i> -DNB			<i>cis,cis</i> -DNB		
	Symmetry	Freq.	Int.	Symmetry	Freq.	Int.	Symmetry	Freq.	Int.
1	b_1	57.4	0.1	a	85.3	0.1	a	77.1	0.2
2	a_2	78.8	0.0	a	127.3	0.2	b	88.1	1.3
3	a_2	147.2	0.0	a	154.3	0.7	a	167.2	2.9
4	a_1	203.6	2.1	a	230.4	2.1	b	188.0	0.8
5	b_1	223.2	1.3	a	262.7	2.9	a	207.1	0.1
6	b_2	289.8	0.0	a	351.3	0.6	b	290.3	6.5
7	b_1	429.6	0.1	a	400.4	0.8	b	383.8	2.8
8	a_1	430.4	0.3	a	446.8	1.2	b	424.5	0.4
9	b_2	445.4	7.3	a	484.3	0.8	a	430.9	1.1
10	a_2	474.2	0.0	a	505.4	0.9	a	532.2	0.1
11	a_1	622.2	8.0	a	624.5	2.2	a	638.2	4.2
12	a_2	710.7	0.0	a	676.1	2.2	b	688.2	5.5
13	b_2	727.2	5.7	a	710.5	10.6	a	690.1	10.8
14	b_1	776.7	55.4	a	754.7	25.9	a	757.7	37.3
15	a_1	795.1	60.6	a	789.1	36.2	b	771.5	51.6
16	b_2	797.7	37.7	a	850.6	9.0	b	850.1	29.8
17	a_2	903.6	0.0	a	883.7	8.8	a	896.1	0.5
18	b_1	988.1	2.3	a	960.2	3.8	b	966.1	3.4
19	a_2	1005.0	0.0	a	992.9	1.9	a	994.5	1.2
20	a_1	1023.6	0.1	a	1021.5	0.5	a	1026.7	1.6
21	b_2	1071.4	21.4	a	1094.6	45.1	b	1077.7	19.7
22	a_1	1085.4	157.0	a	1096.8	26.1	a	1095.2	152.3
23	b_2	1149.8	39.0	a	1160.1	17.8	b	1136.6	13.0
24	a_1	1164.4	5.6	a	1169.9	27.6	a	1161.4	3.5
25	b_2	1248.3	53.2	a	1253.3	1.8	b	1258.9	0.2
26	a_1	1345.0	1.8	a	1337.1	17.9	a	1326.4	29.4
27	b_2	1425.5	65.3	a	1430.1	35.9	a	1427.9	34.7
28	a_1	1458.5	0.7	a	1439.9	42.6	b	1446.0	3.3
29	b_2	1529.1	148.4	a	1481.6	179.2	b	1521.6	80.6
30	a_1	1538.9	115.8	a	1527.2	175.1	a	1555.7	137.9
31	a_1	1596.5	4.2	a	1575.9	0.3	a	1587.7	24.5
32	b_2	1609.1	1.7	a	1598.9	2.8	b	1599.8	4.0
33	b_2	3066.0	3.2	a	3067.9	2.5	b	3068.7	0.5
34	a_1	3079.5	11.0	a	3079.9	3.6	a	3076.6	1.0
35	b_2	3096.6	0.2	a	3087.1	2.5	b	3082.9	4.0
36	a_1	3098.4	8.0	a	3092.5	10.0	a	3090.9	13.7

DNB, dinitrosobenzene.

^a Orientation in space according to IUPAC conventions.²³

The IR spectrum of nitrosobenzene was taken under conditions that help to avoid rapid dimerization. The low concentration of nitrosobenzene needed to achieve these conditions caused very low transmittance or absorbance rates in the resulting spectra. To get an optimum vapor pressure the spectrum was taken at room temperature for the region from 300 to 3200 cm^{-1} and at about 323 K (50°C) for the 40–650 cm^{-1} range. Out of 33 fundamentals of nitrosobenzene within C_s symmetry,

there are 10 out of plane modes (a'') and 23 in-plane ones (a'). All of them are expected to be IR active. Most fundamentals were identified and assigned experimentally by Bradley and Strauss.²² A comparison of our calculated spectrum with the experimentally obtained data is given in Table IV.

In general the agreement between the tabulated spectrum of Bradley and Strauss²² and the calculated spectrum is less satisfactory than for benzo-furoxan. One reason may be the considerable over-

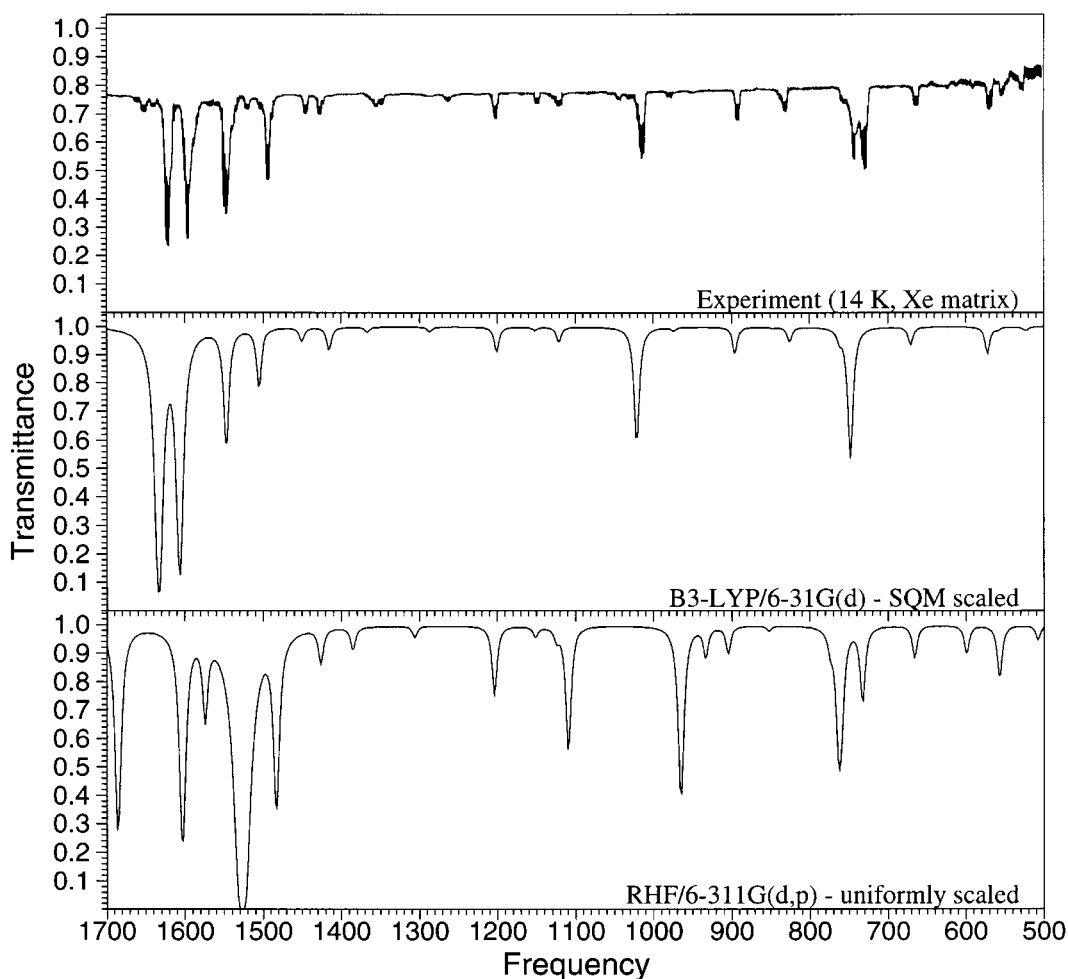


FIGURE 3. Comparison of calculated with experimental vibrational spectra of benzofuroxan. The experimental spectrum of Hacker² has been digitized with permission. © 1995 American Chemical Society.

lap of the rotational wings in the gas-phase spectra. It would be desirable to have access to matrix IR spectra for this molecule. The CCNO torsion calculated at 104 cm^{-1} agrees very well with the experimental value at 101 cm^{-1} . Another very low vibration, the "X bend" (the in-plane bending of the nitroso group), experimentally at 254 cm^{-1} is also in very good agreement with 253 cm^{-1} . There are a few discrepancies between our SQM calculated spectrum and the experimental spectrum, mainly in the region below 1000 cm^{-1} . These vibrations are mostly weak out of plane modes. The largest discrepancy was found for a weak out of plane mode at 200 (expt) and $226\text{ cm}^{-1}\text{ (calcd)}$. A deviation of 26 cm^{-1} leaves doubt whether this vibration was correctly identified; therefore, this band was not considered in the derivation of the new set of scaling factors. All other deviations do not exceed 14 cm^{-1} . The weak boat deformation of

the benzene ring experimentally at 458 cm^{-1} was calculated at 448 cm^{-1} . A similar deviation was found for the corresponding chair deformation, namely 12 cm^{-1} . The medium strong a' band calculated at 674 cm^{-1} has no experimental counterpart in table III of ref. 22. It is likely that it and the $694\text{ cm}^{-1}\text{ (calcd)}$ a'' mode form a Coriolis resonance pair, and both are included in the experimental 682 cm^{-1} band. Two hydrogen out of plane bendings show similar errors: 750 (expt) vs. $760\text{ cm}^{-1}\text{ (calcd)}$ and 933 (expt) vs. $945\text{ cm}^{-1}\text{ (calcd)}$. All calculated vibrations above 1000 cm^{-1} are in excellent agreement with the experiment, with the exception of a medium-strong band at $1334\text{ cm}^{-1}\text{ (calcd)}$ that probably overlaps with the $1310\text{ cm}^{-1}\text{ (calcd)}$; $1314\text{ cm}^{-1}\text{ (expt)}$ band. It may be identical with the very weak feature found at 1348 cm^{-1} , but the intensities do not support this assignment.

Unfortunately, a plot of the experimental spectrum for nitrosobenzene was not included in Bradley and Strauss's article²²; therefore, we had to rely on the approximate description of the intensities by the authors, which makes a correct assignment difficult in some cases. There are discrepancies with the intensities of several bands. The reported strong modes at 254, 850, and 933 cm^{-1} are calculated at 253, 859, and 945 cm^{-1} and are weak.

The new set of scaling factors derived for the molecules of this study reliably reproduces the experimental fundamentals of benzofuroxan and nitrosobenzene. The largest deviation in the range between 500 and 1700 cm^{-1} does not exceed 14 cm^{-1} . The average absolute deviation in the same region is 6 cm^{-1} , including all characteristic modes of the nitroso group and the furazan ring.

Modeling an IR Spectrum of Photolysed Benzofuroxan

We can assume that the scaling factors derived in the previous section also reliably predict spectra for the chemically similar 1,2-dinitrosobenzene conformers. The scaled harmonic fundamentals together with their intensities and symmetry for all three conformers are given in Table V.

Unfortunately, the very intense $\text{N}=\text{O}$ stretching bands in these spectra are rather sensitive to scaling factors, i.e., their position and amplitude varies with changing scaling factors. For instance, after changing the scaling factor for $\text{N}=\text{O}$ stretchings from 0.89 to 0.87, the two $\text{N}=\text{O}$ stretching bands of *trans,trans*-1,2-dinitrosobenzene are shifted from 1529 and 1539 cm^{-1} to 1521 and 1523 cm^{-1} , respectively. Nevertheless, we expect all bands to be accurate to ± 20 cm^{-1} . A comparison of these spectra with the experimental reaction spectrum is shown in Figure 4.

This comparison shows that the contribution of some isomers to the reaction spectrum must be very low. For instance, a significant contribution of *cis,cis*-1,2-dinitrosobenzene is not very likely, because the relatively strong bands at 850 and 1326 cm^{-1} are not present in the matrix spectrum. In addition, the $\text{N}=\text{O}$ stretching band at 1556 cm^{-1} appears 40 cm^{-1} higher than observed by Hacker,² which makes a contribution of this conformer rather improbable. It is more difficult to determine the participation of *cis,trans*-1,2-dinitrosobenzene. The strong $\text{N}=\text{O}$ stretching band at 1482 cm^{-1} in

the calculated spectrum cannot be observed in the experimental spectrum of Hacker,² even if we allow an error of more than 20 cm^{-1} . Moreover, two very intense peaks at 1482 and 1527 cm^{-1} , separated by 46 cm^{-1} , cannot be seen in the reaction spectrum. The distance between these two bands is slightly dependent on the scaling factors, but changing the corresponding factor by 0.02 leads only to a decrease of the separation by 4 cm^{-1} . It is very unlikely that the scale factors are off so much that the two bands should coalesce to the very intense peak at 1520 cm^{-1} in the experimental spectrum. On the other hand the double peak at 1430 and 1440 cm^{-1} can be seen in the experiment, seemingly indicating the presence of this conformer. The conformer that certainly contributes to the reaction spectrum is *trans,trans*-1,2-dinitrosobenzene, because all of its bands can be found in the matrix spectrum.

To find the most likely composition of the reaction spectrum, we introduced a further approximation. We adjusted the intensities of the five most intense bands and the bands at 559 and 572 cm^{-1} in the calculated spectrum of benzofuroxan in such a way that their intensities relative to each other more closely resembled those of the experimental spectrum of benzofuroxan. This guaranteed that the error with respect to the contribution of benzofuroxan in the reaction spectrum was minimized, because now the agreement between the calculated and the experimental spectrum is almost perfect. For identifying the composition of the mixture of the reaction spectrum, we performed a systematic grid search with respect to all four molecules, even though the contribution of some conformers was very unlikely. After we identified the region of best agreement relative to the matrix spectrum, we tried in a heuristic procedure to obtain the best fit. The composition found that way consists of 40% benzofuroxan and 60% *trans,trans*-1,2-dinitrosobenzene, with an estimated error bar of $\pm 10\%$. The modeled spectrum and the experimental one are compared in Figure 5.

Although the overall agreement is good, there are some discrepancies that are discussed below. The most intense $\text{N}=\text{O}$ stretching band is 14 cm^{-1} too high in the calculated spectrum. The shoulder on its violet wing in the matrix spectrum appears as a new peak in the calculated spectrum, separated from the $\text{N}=\text{O}$ stretching band by only 10 cm^{-1} . As shown above, certain changes in the scaling factors can diminish the separation of these two bands to only 2 cm^{-1} . However, all these deviations are within the limits one can expect

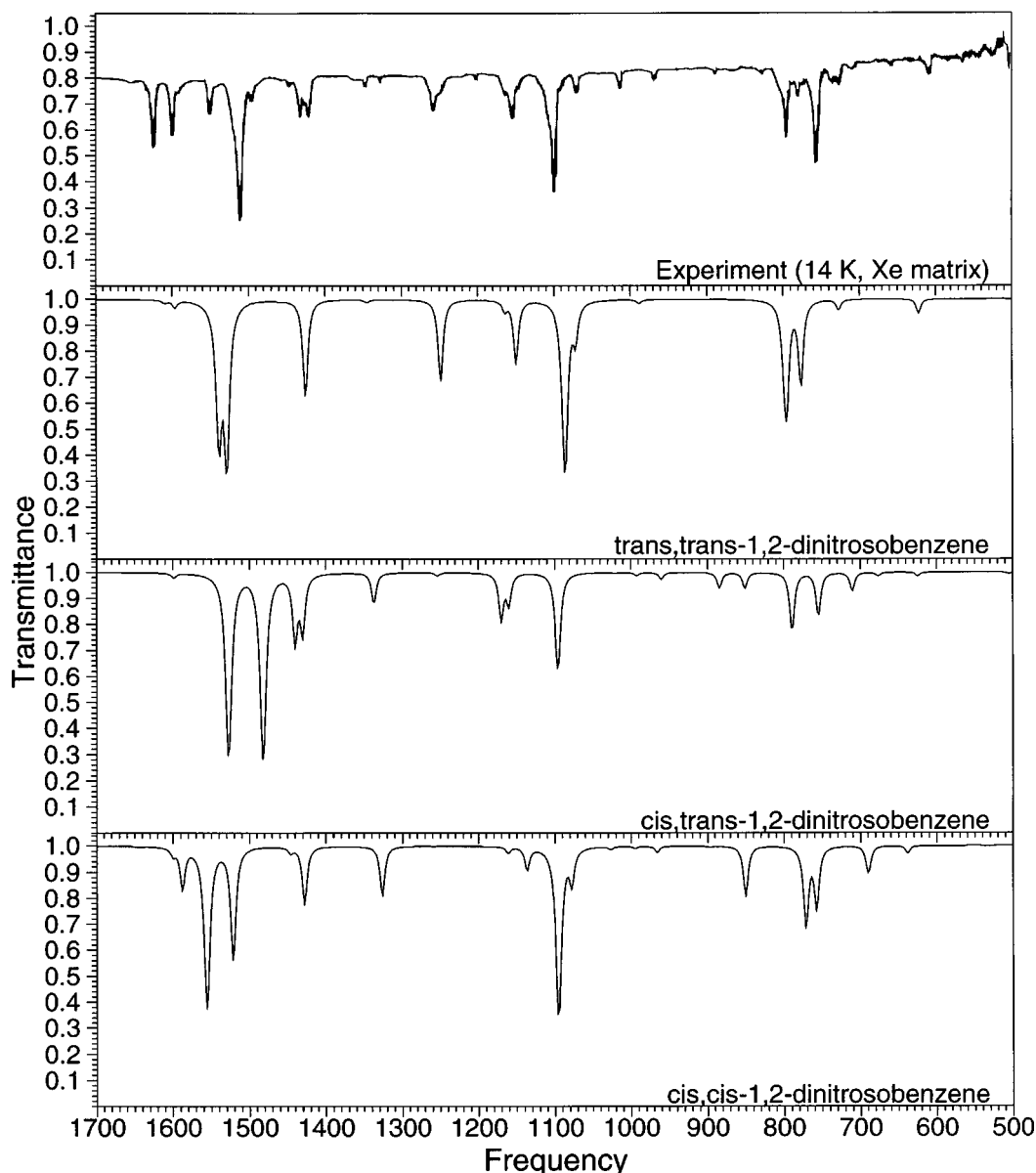


FIGURE 4. Calculated vibrational spectra of conformational isomers of 1,2-dinitrosobenzene in comparison with the experimental reaction spectrum. The experimental spectrum of Hacker² has been digitized with permission.

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from the scaling procedure (see above). On the other hand, there is a problem with the double band at about 1440 cm^{-1} , which appears only in the experimental spectrum. In that region the calculated spectrum shows a strong band with a shoulder, but the shoulder is caused by benzo-furoxan and not by *trans,trans*-1,2-dinitrosobenzene as denoted by Hacker.² The only conformer that shows a double peak in that region is *cis,trans*-1,2-dinitrosobenzene, but its contribution can be excluded by the absence of some of its

strong bands. Looking for combination bands in the spectrum of *trans,trans*-1,2-dinitrosobenzene one finds two possible combinations. Namely, combinations of the fundamentals at 1005 and 430 cm^{-1} as well as 798 and 622 cm^{-1} would yield peaks of b_2 symmetry in exactly this region. Coupling with the band of the same symmetry at 1426 cm^{-1} would also explain the intensity of such a band. However, this is rather speculative and shall not be considered further. Another problem appears in the region near 780 cm^{-1} . While three

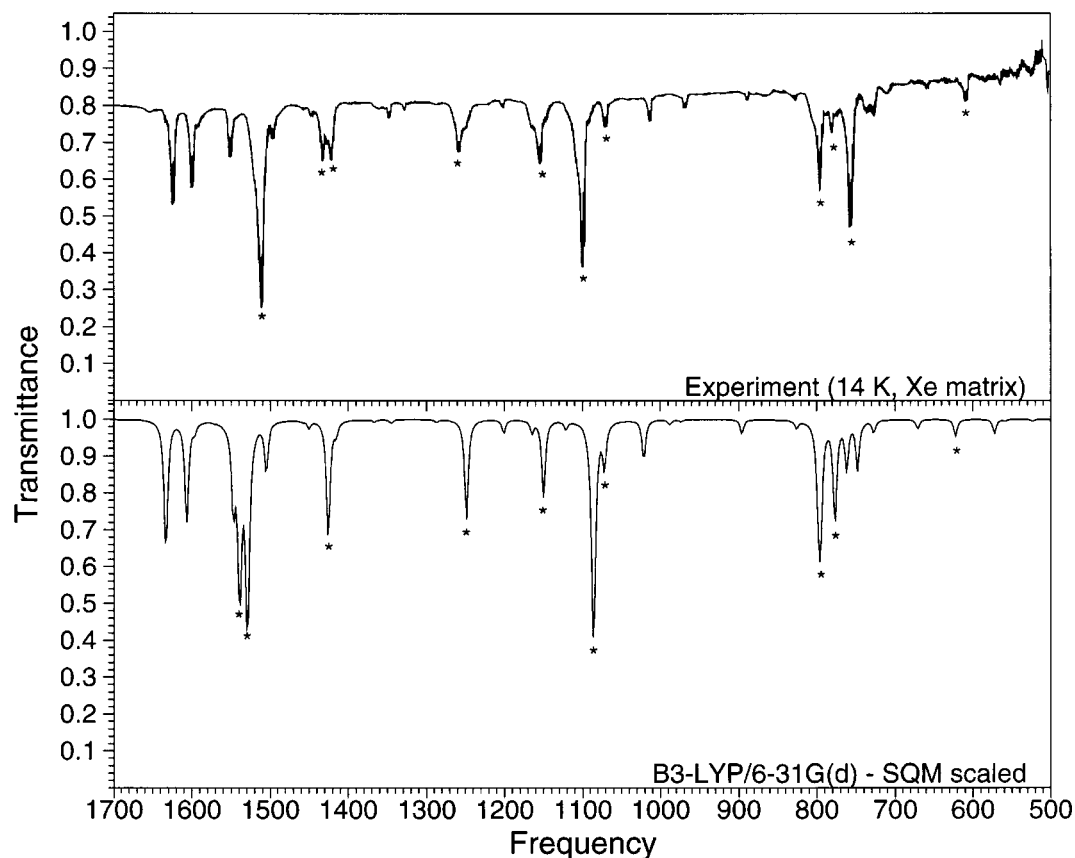


FIGURE 5. Modeled vibrational spectrum of 60% *trans,trans*-1,2-dinitrosobenzene and 40% benzofuroxan in comparison with the experimental reaction spectrum. Peaks assigned to 1,2-dinitrosobenzene are marked by stars. The experimental spectrum of Hacker² has been digitized with permission. © 1995 American Chemical Society.

new bands occur in Hacker's spectrum,² only two (with inverted intensities) can be seen in the model. The calculated spectrum of *trans,trans*-1,2-dinitrosobenzene indeed has three bands in this region, but two of them are separated by only 3 cm⁻¹ and thus appear in the figure as only one band. Note that in a composite spectrum with nearly coincident peaks, small systematic inaccuracies may add and lead to a calculated spectrum that does not match the experimental spectrum as well optically as is the case for a single component. In spite of this, the agreement between the experimental and the model spectrum is quite convincing and therefore one can assume that the only significant contribution is from *trans,trans*-1,2-dinitrosobenzene as assumed by most authors.⁵⁻⁷ This is an interesting result, because the thermal ring opening in benzofuroxan must lead first to *cis,trans*-1,2-dinitrosobenzene (see ref. 7) through a reaction path that corresponds to the 467 cm⁻¹ normal coordinate. Because the two conformers

are almost identical in energy, a simple model would predict that both would be present in the reaction mixture.

Discussion and Conclusions

Based on calculated vibrational force fields, we simulated a composite experimental spectrum that was taken in Xe matrix after photolysing benzofuroxan for 2 h. The only significant contribution (60%) found besides the educt (40%) was *trans,trans*-1,2-dinitrosobenzene. This composition favors a reaction mechanism that resembles the thermal reaction investigated in our previous study,⁷ in which the reaction via *trans,trans*-1,2-dinitrosobenzene is slightly preferred in apolar solvents (mechanism A in ref. 7). However, assuming this mechanism one would also expect a certain contribution of *cis,trans*-1,2-dinitrosobenzene, because the ring opening vibration at 467 cm⁻¹ and

energetic considerations lead to this conformer, but it could not be found from analyzing the IR spectrum. There are several possible explanations for this result, but the most likely is the following: the photochemical reaction probably leads to a certain distribution between *cis,trans*-1,2-dinitrosobenzene and *trans,trans*-1,2-dinitrosobenzene. But because the barrier between *cis,trans*-1,2-dinitrosobenzene and benzofuroxan is only 1.6 kcal/mol [B3-LYP/6-311G(*d, p*) after zero point vibrational energy (ZPE) correction],⁷ excess kinetic energy may cause this conformational isomer to react back to benzofuroxan immediately; therefore, it is not trapped in the cryoscopic experiment. On the other hand the barrier of 5.3 kcal/mol [B3-LYP/6-311G(*d, p*), ZPE corrected] between *trans,trans*-1,2-dinitrosobenzene and *cis,trans*-1,2-dinitrosobenzene is too high to allow an interconversion under these conditions. The same argument explains why no *cis,cis*-1,2-dinitrosobenzene could be seen in the reaction spectrum: the calculated barrier between *cis,cis*-1,2-dinitrosobenzene and *cis,trans*-1,2-dinitrosobenzene is even lower, 0.6 kcal/mol [B3-LYP/6-311G(*d, p*), ZPE corrected] and therefore the *cis,cis* conformer would react immediately via *cis,trans*-1,2-dinitrosobenzene to benzofuroxan. This explanation would support the calculated energetic relations of all intermediates and transition states of the thermal reaction as discussed in our first study.⁷ A final resolution of the initial photo product would require accurate calculations on the conical intersection between the ground and the first excited state. Because of often observed similarities between photochemical and thermal reactions, the result that *trans,trans*-1,2-dinitrosobenzene is involved in the photochemical pathway makes it likely that it is also the intermediate of the thermally induced rearrangement. However, the explanation given above does not conclusively exclude the reaction via *cis,cis*-1,2-dinitrosobenzene, in agreement with the conclusions reached in ref. 7.

We see an important potential application of the procedure described here for the analysis of reaction mixtures solely from computed vibrational force fields. Experimental vibrational (especially IR) spectra of the mixture are usually readily available. However, the spectra of the potential components, often novel or marginally stable compounds, are frequently unknown. If the number of components is reasonably small, a procedure similar to the one described here could be used to identify the components and to determine their relative amounts. Benzofuroxan with its exotic

N—O bonds is probably one of the more difficult cases in organic chemistry. For most organic reactions, a more automated procedure using transferable scale factors¹² should be applicable.

Acknowledgments

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References

1. A review about the chemistry of benzofuroxans is given by A. R. Katritzky and M. F. Gordeev, *Heterocycles*, **35**, 483 (1993).
2. N. P. Hacker, *J. Org. Chem.*, **56**, 5216 (1991).
3. I. R. Dunkin, M. A. Lynch, A. J. Boulton, and N. Henderson, *J. Chem. Soc., Chem. Commun.*, 1178 (1991).
4. S. Murata and H. Tomioka, *Chem. Lett.*, 57 (1992).
5. M. Ponder, J. E. Fowler, and H. F. Schaefer, *J. Org. Chem.*, **59**, 6431 (1994).
6. W. Friedrichsen, *J. Phys. Chem.*, **98**, 12933 (1994).
7. G. Rauhut, *J. Comput. Chem.*, **17**, 1848 (1996).
8. P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, *J. Am. Chem. Soc.*, **105**, 7073 (1983).
9. G. Rauhut and P. Pulay, *J. Am. Chem. Soc.*, **117**, 4167 (1995).
10. A. D. Becke, *Phys. Rev.*, **A38**, 3098 (1988).
11. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, **B41**, 785 (1988).
12. G. Rauhut and P. Pulay, *J. Phys. Chem.*, **99**, 3093 (1995).
13. G. Fogarasi, X. Zhou, P. W. Taylor, and P. Pulay, *J. Am. Chem. Soc.*, **114**, 8191 (1992).
14. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
15. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980).
16. D. Britton and J. M. Olson, *Acta Crystallogr.*, **B35**, 3076 (1979).
17. H. L. Ammon and S. K. Bhattacharjee, *Acta Crystallogr.*, **B38**, 2498 (1982).
18. D. A. Dieterich, I. C. Paul, and D. Y. Curtin, *J. Am. Chem. Soc.*, **96**, 6372 (1974).
19. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, J. S. Gonzales, P. L. Martin, D. J. Defrees, D. J. Baker, J. J. P. Stewart, and J. A. Pople, *Gaussian G92/DFT*, Gaussian Inc., Pittsburgh, PA, 1993.
20. Z. Zhou, Ph.D. thesis, University of Arkansas, 1992.
21. G. Pongor, *SCALE2*, Eötvös L. University, Budapest, 1978.
22. G. M. Bradley and H. L. Strauss, *J. Phys. Chem.*, **79**, 1953 (1975).
23. *J. Chem. Phys.*, **23**, 1997 (1955).